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Dielectric Relaxation of W/O Emulsions in Particular Reference to Theories of Interfacial Polarization

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Dielectric constants and electric conductivities of water-in-oil (W/O) emulsions were measured over a wide range of concentration and at frequencies ranging from 20 Hz to 3 MHz. The W/O emulsions showed striking dielectric relaxation due to interfacial polarization at higher frequencies above 10 kHz. Both the limiting dielectric constants at high and at low frequencies were in better agreement with Hanai's theory than with Wagner's. It was reported in our previous work that limiting dielectric constants of W/O emulsions at high frequencies were decreased remarkably with the increase of shear rate and of agitation of the specimens. No such peculiar effect was observed in the present emulsions which were stabilized by minimal use of emulsifier. It is inferred that the effects of shearing and agitating W/O emulsions on their dielectric constants as previously reported may be due to the use of excessive amount of emulsifiers which are apt to form a surface layer at the water-oil interface.

I INTRODUCTION

It is known from earlier work that a heterogeneous structure of material shows dielectric relaxation, which is considered to be due to interfacial polarization. Among others water-in-oil (W/O) emulsions were studied dielectrically by a number of investigators[1] because of the simple geometry of dispersed particles in spherical shape.

From a theoretical point of view for disperse systems of spherical particles, well-known Wagner's theory[2] was applicable to disperse systems at lower concentrations of the disperse phase. For higher concentrations, Hanai's theory[3] was proposed to explain quantitatively experimental data.

On the other hand, one of the present authors[4] carried out dielectric measurements on W/O emulsions to examine the validity of these theories. According to his results, the W/O emulsions showed remarkable dielectric relaxation due to interfacial polarization, and the limiting dielectric constants at high frequencies were in good agreement with Hanai's theory especially at higher concentrations of more than 40% of the disperse phase. The limiting dielectric constants at low frequencies were always much higher than both values predicted by Wagner's theory and by Hanai's. The more peculiar characteristics on these W/O emulsions were that, on mechanically stirring or shearing the emulsions, the limiting dielectric constants at low frequencies showed remarkable decrease towards the values predicted by Hanai's theory.

In our recent study, it was found that such a kind of peculiar characteristic on the W/O emulsions resulted from the use of excessive amount of emulsifiers. The purpose of the present study is to observe the dielectric behavior of W/O emulsions prepared by minimal use of emulsifier and to discuss the results in the light of the theories.

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II THEORETICAL

When spherical particles of a disperse phase with the dielectric constant ε_i and the electric conductivity κ_i (S/cm) are dispersed in a continuous medium of the dielectric constant ε_a and the electric conductivity κ_a by the volume fraction Φ, the whole system is to show dielectric relaxation which is characterized by the limiting dielectric constants at high frequencies ε_h and at low frequencies ε_l and the limiting conductivities at high frequencies κ_h and at low frequencies κ_l and the relaxation frequency f_0 (Hz), where the disperse phase is very conductive in comparison with the continuous medium, that is, $\kappa_i \gg \kappa_a$. The theoretical expressions are the followings.[3)]

1) Wagner's Theory

$$\varepsilon_h = \varepsilon_a \frac{\varepsilon_i + 2\varepsilon_a + 2\Phi(\varepsilon_i - \varepsilon_a)}{\varepsilon_i + 2\varepsilon_a - \Phi(\varepsilon_i - \varepsilon_a)}, \tag{1}$$

$$\varepsilon_l = \varepsilon_a \frac{1+2\Phi}{1-\Phi}, \tag{2}$$

$$\frac{\kappa_h}{\kappa_i} = \left[\frac{3\varepsilon_a}{\varepsilon_i + 2\varepsilon_a - \Phi(\varepsilon_i - \varepsilon_a)}\right]^2 \Phi, \tag{3}$$

$$\frac{\kappa_l}{\kappa_a} = \frac{1+2\Phi}{1-\Phi}, \tag{4}$$

and

$$f_0 = \frac{\kappa_i(1-\Phi)}{\varepsilon_i + 2\varepsilon_a - \Phi(\varepsilon_i - \varepsilon_a)} \times 1.7975 \times 10^{12}. \tag{5}$$

2) Hanai's Theory

$$\frac{\varepsilon_i - \varepsilon_h}{\varepsilon_i - \varepsilon_a} \left(\frac{\varepsilon_a}{\varepsilon_h}\right)^{1/3} = 1 - \Phi, \tag{6}$$

$$\varepsilon_l = \varepsilon_a \frac{1}{(1-\Phi)^3}, \tag{7}$$

$$\frac{\kappa_h}{\kappa_i} = \frac{3\varepsilon_h(\varepsilon_h - \varepsilon_a)}{(\varepsilon_i + 2\varepsilon_h)(\varepsilon_i - \varepsilon_a)}, \tag{8}$$

and

$$\frac{\kappa_l}{\kappa_a} = \frac{1}{(1-\Phi)^3}. \tag{9}$$

A theoretical expression of f_0 in Hanai's theory is not derived yet.

III EXPERIMENTAL

Preparation of W/O Emulsions

The oil phase for W/O emulsions was a mixture of kerosene and carbon tetrachloride (5 : 2 by volume), and contained Span 80 (0.5% by volume) as an emulsifier. Distilled water was gradually added to the oil phase with vigorously mixing by use of a loose-fitting Teflon-glass homogenizer. The particle size of water droplets was in a range of 10 to 18 μm in diameter.

Measuring Cell

The measuring cell consisted of two concentric platinum cylinders whose empty capacitance was about 3.8 pF. The cell constant was determined accurately by several standard liquids. The measurements were made at 25°C.

Dielectric Measurements

Both the capacitance and the conductance were measured over a frequency range of 20 Hz to 3 MHz with a TR-1BK Ratio Arm Transformer Bridge made by Ando Electric Co., Ltd.

IV RESULTS AND DISCUSSION

In our previous experiment[4] the concentration of emulsifiers in oil phase was 5%, which was found in the present experiment to be a sufficiently high concentration to give rise to some peculiar characteristics such as the considerably high values of dielectric constants in comparison with the theoretical prediction and the decrease of dielectric constants on stirring. On reducing the concentration of the emulsifiers down to 1%,

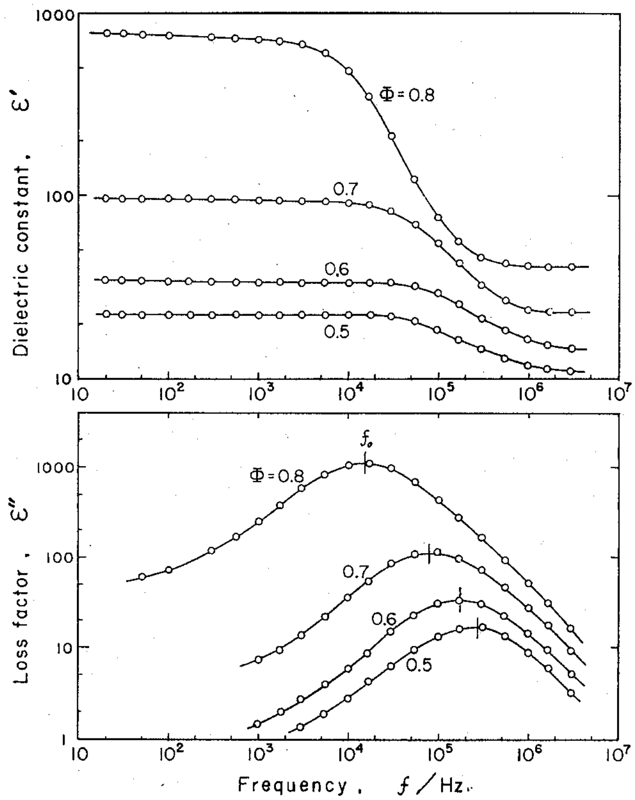

Fig. 1. Frequency dependence of dielectric constants ε' and loss factors ε'' for the W/O emulsions of 80, 70, 60, and 50% in volume concentration Φ at 25°C.

we found no stirring effect on the dielectric constants. Hence, in the present experiment, we adopted a concentration 0.5% of Span 80 in the oil phase, the concentration being still sufficient to keep stability of the emulsions prepared.

In Figs. 1 and 2 is shown the frequency dependence of dielectric constant ε', loss factor ε'' and electric conductivity κ for the W/O emulsions in various concentrations. All the values observed showed no change on agitation or on flow of the specimens. The striking dielectric relaxation as seen in Figs. 1 and 2 may be attributed to the interfacial polarization which was discussed theoretically in the previous paper.[3)]

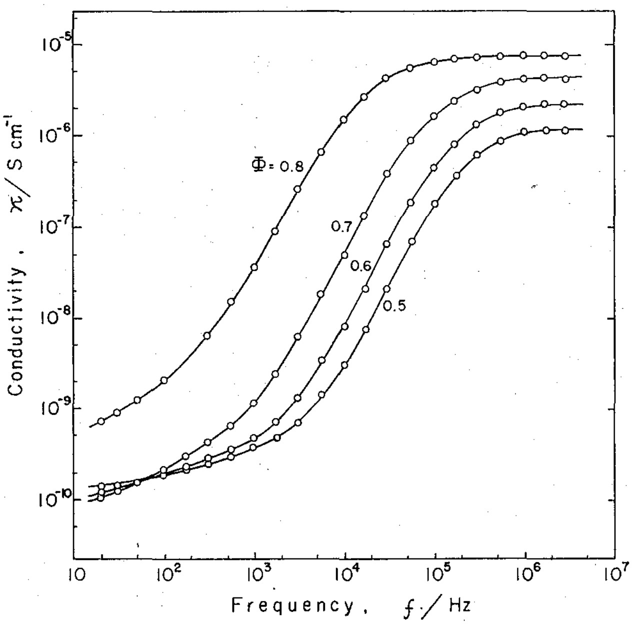

Fig. 2. Frequency dependence of electric conductivities κ for the W/O emulsions of 80, 70, 60, and 50% in volume concentration Φ at 25°C.

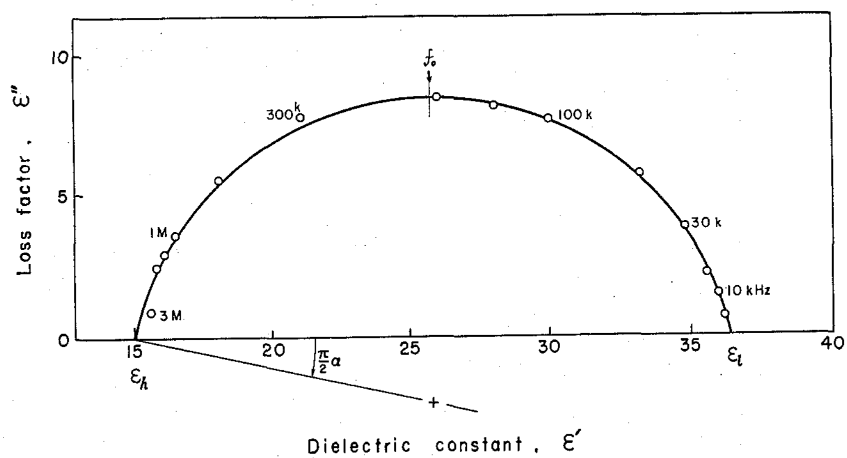

Fig. 3. Complex plane plots of ε' and ε'' for the W/O emulsion of 60% in volume concentration at 25°C.

Complex plane plots of ε' and ε'' for the W/O emulsion of 60% gave a circular-arc as shown in Fig. 3. Hence the present dielectric relaxation can be represented as a function of frequency f in the form

$$\varepsilon'-j\varepsilon''=\varepsilon_h+\frac{\varepsilon_l-\varepsilon_h}{1+(jf/f_0)^{1-\alpha}}, \tag{10}$$

where ε_h and ε_l are the limiting values of ε' at high and low frequencies respectively, f_0 the relaxation frequency and α denotes a parameter for the distribution of relaxation frequencies and $j=\sqrt{-1}$. The dielectric parameters ε_h, ε_l, f_0, and α can be determined from Figs. 1, 2, and 3. The W/O emulsions in other concentrations gave plots similar to those shown in Fig. 3.

In Table I are summarized the values of such parameters for the W/O emulsions at various concentrations. Since the dielectric relaxation shifted to higher frequencies with

Table I. Values of ε_h, ε_l, κ_h, f_0, and α for the W/O Emulsions at Various Concentrations Φ

Volume fraction of disperse phase Φ	ε_h	ε_l	κ_h in 10^{-6} S/cm	f_0 in kHz	α
0.1	—	2.99	—	—	—
0.2	—	4.00	—	—	—
0.3	5.34	6.43	0.46	1050	0.111
0.4	7.74	10.8	0.69	750	0.030
0.5	10.9	18.3	0.92	320	0.167
0.6	15.0	36.4	2.31	174	0.135
0.7	23.4	94.5	4.63	78.0	0.093
0.8	40.4	750.	7.64	15.5	0.127

Oil phase: Dielectric constant $\varepsilon_a=2.10$, conductivity $\kappa_a=6.55\times10^{-11}$ S/cm
Water phase: Dielectric constant $\varepsilon_i=77.5$, conductivity $\kappa_i=2.45\times10^{-5}$ S/cm

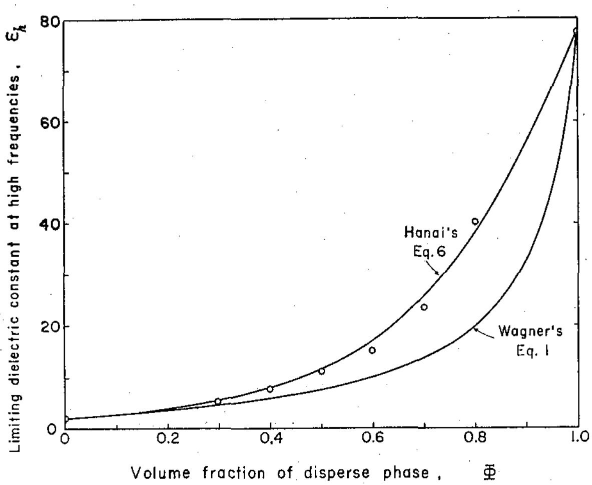

Fig. 4. Concentration dependence of limiting dielectric constant at high frequencies ε_h for the W/O emulsions at 25°C.

decreasing concentration, it was difficult to determine the values of f_0 and κ_h with accuracy for lower concentrations of less than 20%.

Limiting Dielectric Constant at High Frequencies ε_h

In Fig. 4, the theoretical values calculated from Eqs. (1) and (6) are compared with the observed values of limiting dielectric constant at high frequencies ε_h. The observed values are much closer to the theoretical curve by Hanai's Eq. (6) than to that by Wagner's Eq. (1) over the whole range of concentration.

Limiting Dielectric Constant at Low Frequencies ε_l

Unlike the previous observation[4] that the limiting dielectric constant at low frequencies ε_l decreased with increasing flow rate of the specimens, the values of ε_l in the present experiment showed values characteristic of the concentration of the disperse phase irrespective of the flow rate. Figure 5 shows the comparison of the observed values of ε_l with the theoretical curves by Hanai's Eq. (7) and Wagner's Eq. (2). Evidently the observed values are very close to Hanai's Eq. (7).

For reference, the observed values of ε_l reported in the previous paper[4] are plotted in Fig. 5. These values which are subject to the flow effect decrease reasonably towards the values obtained by the present experiment with increasing flow rate.

Limiting Conductivity at High Frequencies κ_h

The values of limiting conductivity at high frequencies κ_h are shown in Fig. 6 against

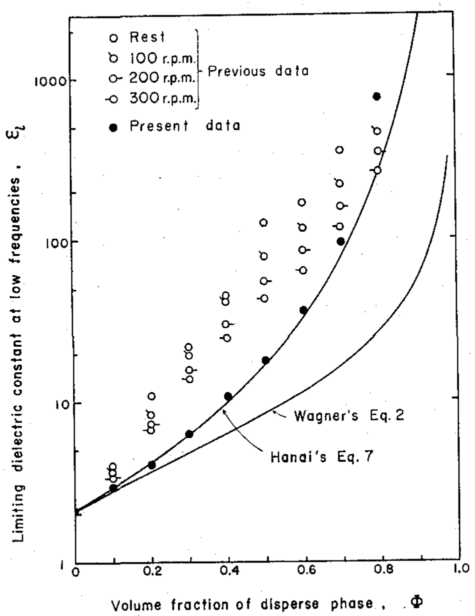

Fig. 5. Concentration dependence of limiting dielectric constant at low frequencies ε_l for the W/O emulsions at 25°C.

For reference, previous data are also shown on ε_l at rest and at various r.p.m. of the cup as a measure of the flow effect reported in Reference 4.

the volume fraction of the disperse phase together with curves calculated from Hanai's Eq. (8) and Wagner's Eq. (3). Since the direct measurement is not possible on the effective electric conductivity of the disperse phase after emulsification, a value $\kappa_i = 2.45 \times 10^{-5}$ S/cm is assumed to draw the theoretical curves. This numerical value for κ_i seems to be reasonable in view of a value 1.6×10^{-6} S/cm for the distilled water measured prior to emulsification. In Fig. 6, the observed values appear to be expressed better by Hanai's Eq. (8) than by Wagner's Eq. (3).

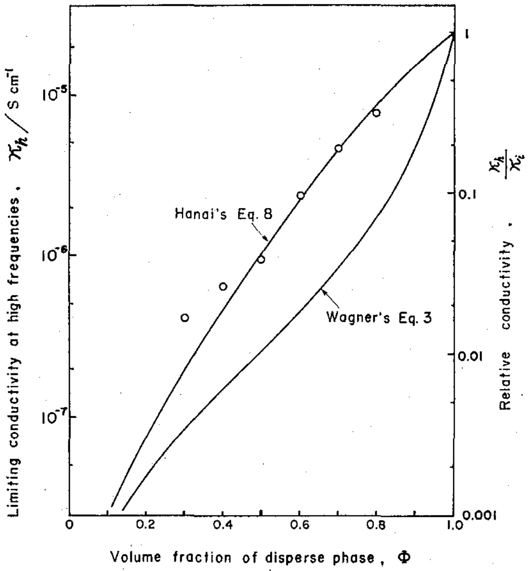

Fig. 6. Concentration dependence of limiting conductivity at high frequencies κ_h for the W/O emulsions.

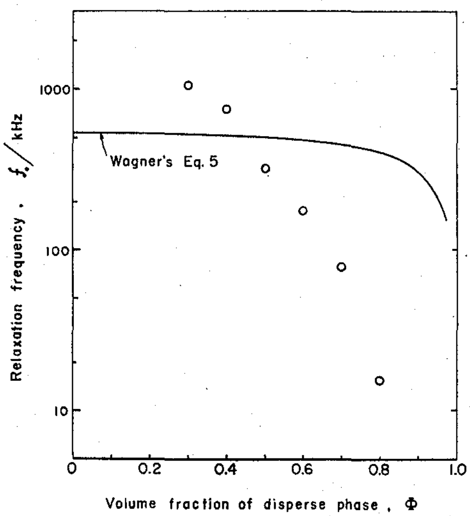

Fig. 7. Concentration dependence of relaxation frequency f_0 for the W/O emulsions. The curve in the figure is calculated from Wagner's Eq. 5.

Dielectric Relaxation Frequency f_0

By use of the values $\kappa_i = 2.45 \times 10^{-5}$ S/cm which was assumed in drawing the theoretical curves in Fig. 6, the dielectric relaxation frequency f_0 can be calculated from Wagner's Eq. (5). Figure 7 shows the comparison of observed values of f_0 and the theoretical curve by Eq. (5). The observed values of f_0 are found to show considerable deviations from the theoretical curve. Unfortunately a theoretical expression of f_0 is not derived yet in Hanai's theory, comparison between the theories being impossible. By the use of salt solutions in definite concentrations, the values of κ_i may be controlled experimentally enough to develop some closer discussion. In such instances, however, the relaxation frequencies can not be measured owing their shift to higher frequencies beyond the present measurements.

V CONCLUSIONS

The W/O emulsions which were stabilized by minimal use of the emulsifier showed striking dielectric relaxation due to interfacial polarization, the relaxation characteristics being unaffected by shearing flow and agitation of the specimens. The limiting dielectric constants at high and low frequencies are satisfactorily represented by theoretical expressions proposed by Hanai.

It is inferred that the effects of shearing and stirring W/O emulsions on their dielectric properties as previously reported may be due to the use of excessive amount of emulsifiers which are apt to form a surface layer at the water-oil interface. Further investigation should be undertaken to elucidate the details of such characteristics due to emulsifiers.

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